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ACID-RESISTANT ARTICLES MADE OF GRANODIORITE, FELSITE, AND BUSKUL'SKOE CLAY

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The phase transitions that take place in firing of clay from the Buskul'skoe deposit, granodiorite from the Severskoe deposit, and felsite from the Pokrovskoe deposit and mixed clays with granodiorite and felsite in different ratios were investigated. The change in the content of crystalline phases (cristobalite, mullite, and quartz) in the initial materials and blends during firing was established by quantitative x-ray phase analysis.

We know [1] that the chemical and mineral composition of the clays used in production of acid-resistant ceramics affects the phase composition and properties of the finished articles. After firing, mullite, quartz, and cristobalite are the basic crystalline phases. The impurities in the clays form a liquid phase on firing which turns into glass on cooling. Cristobalite from these crystalline phases worsens the properties of the finished articles to the greatest degree. In firing of kaolinite – hydromica clays, cristobalite is almost not formed. For this reason, mineral fluxes that form a melt at a low firing temperature are added to the batch to improve the properties of acid-resistant articles made of kaolinite and kaolinite-montmorillonite clays, and this favors sintering and dissolution of the amorphous silica separated as a result of decomposition of clay minerals.

The phase transitions that take place on heating in batches containing Buskul'skoe clay, Pokrovskoe clay and Severskoe granodiorite were investigated. The chemical and mineral compositions of the initial materials are reported in Tables 1 and 2.

According to the results of chemical, x-ray phase, and differential thermal analyses, Buskul'skoe clay is a kaolinite clay and according to some data, it is a kaolinite-montmorillonite clay. The composition of the plagioclases contained in granodiorite is close to the composition of oligoclase, and hornblende is close to pargasite. The orthoclase contained in the felsite is transformed into microcline when heated above 1000°C.

The phase changes that take place on heating felsite and granodiorite were investigated by high-temperature x-ray phase analysis at 50, 170, 270, 450, 580, and 950°C. In addition, XPA was performed on samples fired at 1000, 1050, 1100, 1150, and 1200°C and the content of the basic phases was determined: mullite, quartz, and cristobalite.

The dependence of the content of crystalline phases (quartz, mullite, and cristobalite) on the firing temperature of

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TABLE 1

Component	Mass content, %									$SiO_{2(fr)}$,* %
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	calcination loss	
Buskul'skoe clay	49.02	32.82	3.01	0.65	0.67	Not determined	0.66	0.66	12.47	18.3
	56.00	37.50	3.44	0.74	0.77	Same	0.75	0.75	–	
Granodiorite	65.92	15.26	3.67	4.05	1.89	0.45	1.75	5.82	0.86	20.0
	66.68	15.43	3.71	4.10	1.91	0.45	1.77	5.88	–	
Felsite	75.93	13.17	1.32	0.24	0.05	0.06	3.84	3.53	1.93	35.0
	77.42	13.43	1.35	0.24	0.05	0.06	3.91	3.60	–	

* Free quartz.

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TABLE 2

Component	Mass content, %											
	quartz	albite	anorthite	orthoclase	hornblende	pyrite	limonite	hydromica	iron hydroxides	kaolinite	montmorillonite	mixed-layer formations
Granodiorite	18 – 22	46 – 30	9 – 11	10 – 12	14 – 25	Under 1	–	–	–	–	–	–
Felsite	35 – 40	28 – 31	–	22 – 25	–	–	Under 2	–	–	1 – 7	–	–
Buskul’skoe clay	18	Under 2	Under 2	Under 2	–	–	–	3 – 5	Under 2	60 – 65	3 – 5	12 – 15

the clay, felsite, and granodiorite is shown in Fig. 1. The theoretical content of mullite in firing Buskul’skoe clay, calculated with the data from chemical analysis, was 46.6 – 52.2%,[2] and was 3 – 5% in firing of felsite. With an increase in the firing temperature, the cristobalite and mullite content increased, while the quartz content decreased due to its conversion into cristobalite and dissolution in the melt formed. Cristobalite was also formed from the amorphous silica separated in decomposition of kaolinite.

It follows from the XPA data on granodiorite at fixed temperatures of 50, 170, 270, 450, 580, and 950°C that the oligoclase and hornblende (pargasite) content at 950°C decreased insignificantly, while the quartz content remained unchanged. On heating above 1000°C, the amount of oligoclase and pargasite decreased, which indicates that they melted. The quartz content decreased in the 1000 – 1150°C range due to its dissolution in the melt.

The color of the material changed in firing of granodiorite: dark brown at 1000°C, dark brown at 1100°C, black at 1150°C.

Mullite and cristobalite were absent in the samples of granodiorite fired in the 1000 – 1200°C range. The free quartz content in natural granodiorite was 21% and decreased to 5% on heating to 1200°C.

XPA of felsite at fixed temperatures of 50, 170, 270, 450, 580, and 950°C showed that at 950°C, the albite content decreased, indicating that it melted. The amount of orthoclase and quartz changed insignificantly. After firing at 1100°C, albite and orthoclase were almost not detected in samples of felsite. In all probability, these minerals were converted into a melt at this temperature. The quartz content was 38% in natural felsite. In firing samples of felsite in the 1000 – 1200°C range (see Fig. 1), the quartz content decreased from 29 to 17% due to its dissolution in the melt formed in melting of albite and orthoclase. In heating above 1000°C, a small amount of mullite (3 – 4%) was formed in felsite. Cristobalite was not detected in samples of felsite fired in the 1000 – 1200°C range.

After heating at 1000°C, felsite was dark brown with a pinkish tint; it was brown with a reddish tint at 1050°C, brown at 1100°C, and light brown to cream at 1150°C.

In firing of Buskul’skoe clay in the 1100 – 1200°C range, 12 – 20% cristobalite and 36 – 39% mullite were formed and the amount of quartz decreased from 11 to 4%. It was found that a liquid phase appeared in firing of granodiorite and felsite at 950°C. For granodiorite, this was due to melting of oligoclase and hornblende and for felsite, to melting of albite. Quartz actively dissolved in the melt formed. In the 1000 – 1200°C range, its content decreased from 16 to 6% in granodiorite and from 28 to 18% in felsite.

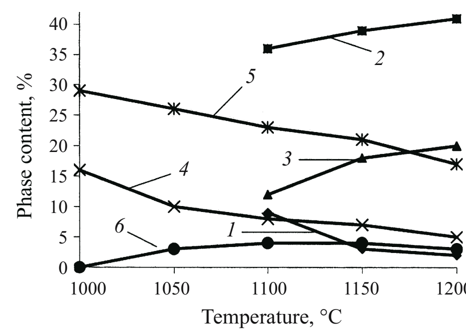

Fig. 1. Phase content in clay [*1*) quartz, *2*) mullite, *3*) cristobalite], granodiorite [*4*) quartz], and felsite [*5*) quartz, *6*) mullite] as a function of the firing temperature.

The effect of the granodiorite or felsite content in the batch on the properties of the samples and phase formation in firing were investigated in compositions with a 0 to 100% content of these components with a step of 20%. The batch compositions are reported in Table 3.

TABLE 3

Batch	Mass content, %		
	Buskul’skoe clay	granodiorite	felsite
Gl	100	–	–
G20	80	20	–
G40	60	40	–
G60	40	60	–
G80	20	80	–
Gr	0	100	–
F20	80	–	20
F40	60	–	40
F60	40	–	60
F80	20	–	80
F	0	–	100

[2] Here and below: mass content.

TABLE 4

Batch	Mass content, %							$SiO_{2(fr)}$,* %	Sum of fluxes, %
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O		
Gl	56.04	37.52	3.44	0.74	0.77	0.75	0.23	21.04	5.93
G20	58.35	32.64	3.50	1.48	1.02	0.98	1.47	20.85	8.45
G40	60.55	28.00	3.55	2.18	1.26	1.19	2.66	20.67	10.84
G60	62.63	23.59	3.60	2.85	1.49	1.39	3.78	20.49	13.12
G80	64.61	19.39	3.65	3.48	1.70	1.58	4.85	20.33	15.27
Gr	66.50	15.39	3.70	4.09	1.91	1.77	5.87	20.17	17.34
F20	60.28	32.69	3.02	0.64	0.63	1.38	0.90	24.00	6.58
F40	64.57	27.87	2.60	0.54	0.48	2.01	1.58	26.95	7.22
F60	68.85	23.06	2.19	0.44	0.34	2.65	2.25	29.89	7.86
F80	73.14	18.24	1.77	0.34	0.19	3.28	2.93	32.84	8.50
F	77.42	13.43	1.35	0.24	0.05	3.91	3.60	35.79	9.15

* Free quartz.

The initial 5 – 0 mm fraction granodiorite and felsite powders were individually dry ground until everything passed through a No. 05 sieve. After careful dry mixing of the clay with the granodiorite and felsite, the batch was moistened with water and mixed again. Cylindrical samples 36 mm in diameter and 12 – 15 mm high were molded from the prepared paste at a pressure of 30 MPa. The samples were dried at 100 – 105°C. The samples were fired at 1000 – 1200°C with a 50°C interval. The physicoceramic properties were determined in the samples obtained and the mullite, quartz, and cristobalite contents were determined by quantitative XPA.

The calculated chemical composition of the batch is reported in Table 4. The sum of fluxes is represented by the following oxides: $Fe_2O_3 + R_2O + RO$. It follows from the data in Table 4 that the oxide-flux content increases from 5.93 to 17.34%, the silica content increased from 56.04 to 66.50%, and the alumina content decreased from 37.52 to 15.39% with an increase in the granodiorite content in the batch. The free quartz content in the batch almost did not change. The flux and silica content also increased with an increase in the amount of felsite in the batch, but to a smaller degree than in the batches with granodiorite — from 5.93 to 9.15 and from 56 to 77.42%, respectively. The quartz content increased from 21.05 to 35.79% while the alumina content decreased from 37.52 to 13.43%.

The alkali-earth oxide and Fe_2O_3 content in the batch also increased from 1.51 to 6.00 and from 3.44 to 3.77%, respectively, on addition of granodiorite, while it decreased from 1.51 to 0.29 and from 3.44 to 1.35% on addition of felsite.

The physicoceramic properties of the fired samples are reported in Table 5.

Batches of all compositions sintered intensively in the 1000 – 1100°C region. Batches containing more than 20% granodiorite sintered most intensively, and they had water absorption of approximately 0% at 1150°C. The water absorption of Buskul'skoe clay fired at this temperature was 1.1%. In firing of samples containing more than 60% granodiorite, the samples swelled at temperatures above 1150°C, and signs of burn-out (melting, dark color) appeared in the samples. The density of samples of Gl, G20, and G40 compositions increased up to 1200°C in firing. In firing of samples based on granodiorite (composition Gr), the maximum density, equal to 2.51 g/cm^3, was attained at a temperature of 1100°C. Further increasing the temperature caused the samples to swell and as a consequence, the density decreased sharply to 2.00 g/cm^3.

Batch compositions with a greater than 80% felsite content sintered most intensively. At 1150°C, the samples with a less than 60% felsite content sintered to less than 1% water absorption, and at 1200°C, the water absorption was equal to 0. The maximum density, equal to 2.36 g/cm^3, was attained in firing of samples based on felsite (composition F) at 1100°C. The samples swelled when the temperature was increased further.

The dependence of the acid resistance of the materials containing granodiorite and felsite on the firing temperature is shown in Fig. 2, which can be used to establish the temperature range in which the acid resistance of the materials is greater than 98%. Increasing the granodiorite and felsite content in the batches decreased the temperature of attaining the acid-resistant state (See Fig. 2*a*). For the initial granodiorite, the region of the acid-resistant state was 1040 – 1188°C; it was 1055 – 1195°C for felsite, and above 1170 – 1180°C for clay. The compositions with 50% clay and 50% granodiorite or felsite had the smallest range of the acid-resistant state. Batches containing felsite had a wider range of the acid-resistant state in comparison to granodiorite.

The results of determining the quartz, cristobalite, and mullite content by quantitative XPA for batches of clay –

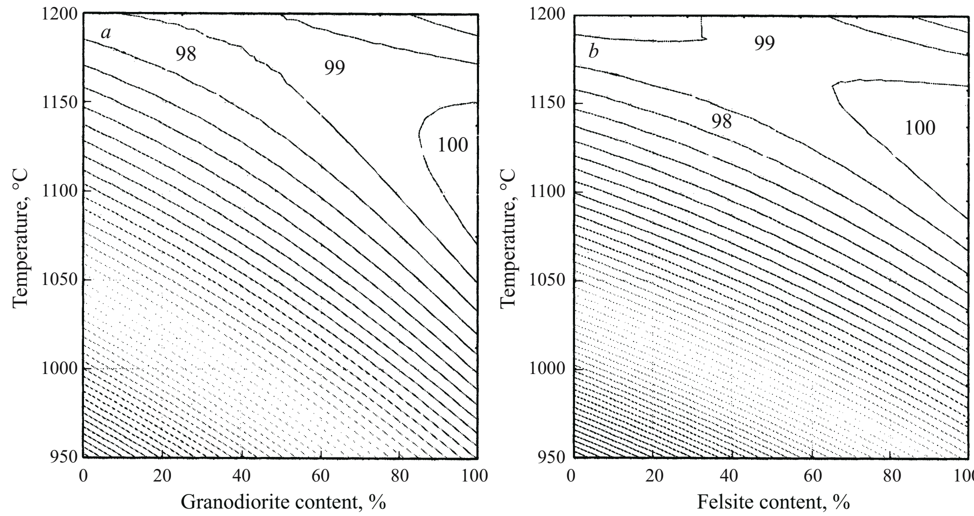

Fig. 2. Projection of the curvilinear surface of the dependence of the acid resistance (%) of batches of clay – granodiorite (*a*) and clay – felsite (*b*) composition on the firing temperature and granodiorite or felsite content in the batch.

granodiorite and clay – felsite compositions are shown in Fig. 3.

With an increase in the firing temperature, the amount of quartz decreased in all samples due to its dissolution in the

TABLE 5

Batch	Firing temperature, °C	Properties of fired samples		
		open porosity, %	water absorption, %	apparent density, g/cm^3
Gl	1000	25.4	12.9	1.97
	1050	16.1	7.4	2.18
	1100	7.7	3.3	2.34
	1150	2.6	1.1	2.45
	1200	0.5	0.2	2.50
G20	1000	21.3	10.0	2.12
	1050	13.5	5.8	2.29
	1100	4.8	2.1	2.29
	1150	2.1	0.9	2.39
	1200	2.5	0.6	2.51
G40	1000	23.1	11.1	2.07
	1050	17.4	7.6	2.19
	1100	6.6	2.8	2.36
	1150	1.2	0.5	2.44
	1200	8.1	3.3	2.44
G60	1000	27.5	13.6	1.97
	1050	22.8	11.0	2.07
	1100	9.5	4.2	2.29
	1150	0.6	0.2	2.33
	1200	Samples were deformed		
G80	1000	32.9	18.1	1.83
	1050	28.8	15.3	1.91
	1100	11.6	5.2	2.23
	1150	0.7	0.3	2.31
	1200	Samples were deformed		
Gr	1000	35.5	19.8	1.79
	1050	30.0	15.4	1.95
	1100	2.0	0.6	2.51
	1150	Samples were deformed		
	1200	Same		
F20	1000	21.3	10.4	2.04
	1050	11.9	5.3	2.24
	1100	5.5	2.3	2.35
	1150	2.1	0.9	2.45
	1200	0.3	0.1	2.49
F40	1000	22.9	11.5	1.99
	1050	13.8	6.4	2.17
	1100	8.7	3.9	2.26
	1150	4.6	1.9	2.38
	1200	3.0	1.2	2.41
F60	1000	25.5	13.3	1.92
	1050	15.3	7.2	2.12
	1100	7.5	3.3	2.27
	1150	3.4	1.4	2.39
	1200	0.4	0.2	2.24
F80	1000	29.3	16.2	1.81
	1050	15.6	7.4	2.10
	1100	0.9	0.4	2.38
	1150	0.2	0.1	2.28
	1200	0.3	0.1	1.75
F	1000	31.9	18.3	1.74
	1050	21.6	11.0	1.97
	1100	0.1	0.0	2.36
	1150	0.0	0.0	2.15
	1200	1.0	0.5	1.78

* See Table 3 for batch composition.

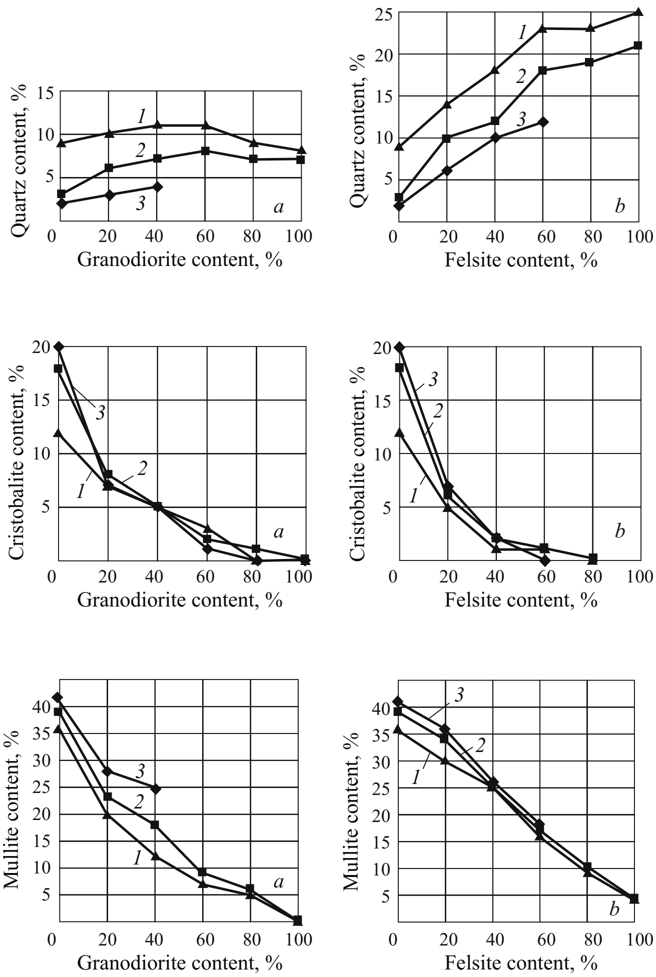

Fig. 3. Quartz, cristobalite, and mullite content in samples with granodiorite (*a*) and felsite (*b*) after firing at 1100°C (*1*), 1150°C (*2*), and 1200°C (*3*).

melt. Clay is the source of formation of cristobalite. Incorporation of granodiorite or felsite in the batches decreased the cristobalite content by more than two times, especially when more than 20% was added, up to total dissolution of cristobalite. Signs of burn-out were then observed in the samples.

Addition of both granodiorite and felsite to the clay batch thus reduces the sintering temperature of the material (by 50 – 100°C) and the firing temperature at which greater than 98% acid resistance is attained and decreases formation of cristobalite. Incorporation of these materials in an amount greater than 40% also reduces the range of the sintered state. This behavior of the batches is due to the appearance of a less viscous melt in the samples with granodiorite in comparison to felsite, since the oxide flux content in granodiorite is 17.34% versus 9.15% in felsite (see Table 2), so that the samples with granodiorite are characterized by a narrower sintering range than the samples with felsite. For this reason, the samples with granodiorite have lower acid resistance than the samples with felsite [1, 2].

Incorporation of granodiorite or felsite causes formation of a melt in which quartz is dissolved at low firing temperatures, which makes the glass phase rich in silica and increases the acid resistance of the samples. In the initial unfired granodiorite and felsite, the quartz content is 20 and 40%, respectively, while the amount of quartz decreases and is 5 – 10% in the samples containing 20% granodiorite or felsite and fired at 1150 – 1200°C. In incorporation of felsite in the batch, a glass phase with a higher silica content and consequently higher viscosity and acid resistance is thus formed.

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